# WATER FROM THE TIMOK RIVER IN SERBIA: ESTIMATION OF ITS SUITABILITY FOR ARABLE SOIL IRRIGATION

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## Abstract

This paper presents the results of analysis of the content of hazardous and harmful substances in the water for irrigation, sampled during the vegetation season 2012/2013 in the basin of the Timok River, from Knjaževac to Visočni hill (Mokranja). The investigation was carried out in three cycles of monitoring on 17 selected sites, which gravitate on the an arable soil that was irrigated. During the mentioned period in the water samples it was determined the values of pH (potentiometrically), ECw (conductiometrically), TDS (gravimetrically); determination of the content of trace elements and heavy metals Cr, Ni, Pb, Cu, Zn, Cd, B, As and Fe was done according to ICP methodology, using ICAP 6300 ICP optical emission spectrometer; heavy metal Hg was determined by a flame atomic adsorption analyzer SensAA Dual.

The content of trace elements and heavy metals in the samples of water is generally below the maximum allowable concentration (MAC), except in one sample, during the first cycle of sampling, where it was recorded increased Cu content, exceeding the recommended limits (0.2509 mg $l^{-1}$). One water sample from the Timok River, sampled in the second cycle of monitoring, showed a slight increase in the Ni content above the recommended limits (0.124 mg $l^{-1}$). Since the location of this sample was also in the vicinity of the village, the assumption is that it is caused by an anthropogenic activity. Based on the obtained data of the content of hazardous and harmful substances in the water for irrigation of the Timok River, it can be concluded that the water is usable for irrigation of agricultural crops and soils, with frequent quality checks during the summer months.

## Introduction

The scope of the research conducted in this paper is the study of quality of irrigation water from the Timok River, complies with the requirements of FAO, 1954 and U.S. Salinity Laboratory classification [8], designed for usability evaluation of irrigation water. Irrigation means the artificial feeding water into the soil in order to rhizosphere wetting layer at a time when the amount of available soil moisture is insufficient to meet the optimum energy crops. Irrigation is a hydro reclamation measure that aims to improve the physical properties of the soil by adding water to achieve an optimum moisture during the growing season and thus achieve optimum yield. It may be applied during part of the growing season or during the growing season. Irrigation of cultivated plants on arable soils involves the use of water of appropriate physical, chemical and biological properties, so it is very important to examine the quality of water used for its intended purpose in order to assess the impact on soil and plants. Intensification of irrigation depends primarily on the provision to the required amount of water of adequate quality. The major pollutants of surface water in the country are industrial enterprises, farms and settlements with sewage systems, without built facilities for waste water treatment, and such with acting, but technically outdated [18]. Anthropogenic impacts and natural processes can affect the quality of surface waters and threaten their use as drinking water, and for use in industry, agriculture, and for other purposes [6,15,22]. The accumulation of metals in an aquatic environment has direct consequences to man and ecosystem [12]. The aim of this study is to assess the current water quality of the Timok River to be used for irrigation of an arable soil near the streams and highlight the pollution risk. Pollution risks are mainly the direct consequence of the discharge of waste water from industrial plants, agricultural intensification or anthropogenic factors. Relief of Timok basin is characterized by a variety of forms resulting from the highly complex genesis and evolution of this area. The formation of the relief was influenced by tectonic processes, volcanic eruptions, sea, lake and river flows. The effect of these forces is protracted and squeezing through many geological periods. The whole area is inclined towards the north and is exposed to the influence of the continental climate of the Pannonia, while the south and east sides surrounded by high mountain ranges, and to the west by high and medium-high mountains. Based on that, several special units in this area can be extracted, varying in altitude, soil and environmental conditions for the development of agriculture [2]. Agricultural soils that have the greatest significance in the observed region are Vertisols with its subtypes and varieties, Eutric Cambisols, brown soils (Distric Cambisols), which are formed on different geological substrates, Fluvisols and Luvisols [23].

**Experimental**

Timok River flows through the Republic of Serbia, and the last 15 km represents the boundary between Serbia and Bulgaria. Estuary is located at an altitude of 28 m, which is the lowest point in the Republic of Serbia. Timok is part of the Black sea basin, with an average flow rate of 24 $m^3s^{-1}$, and the maximum that can be 40 $m^3s^{-1}$. In geographical terms Timok River basin lies between $43^o30'$ and $44^o45'$ north latitude and $19^o30$ 'and $20\ ^o30'$ east longitude (Figure 1).


| Sampling point | Easting | Northing | Sampling point | Easting | Northing |
|---|---|---|---|---|---|
| 1 | 7628790 | 4889690 | 10 | 7604960 | 4844430 |
| 2 | 7627190 | 4886910 | 11 | 7603970 | 4841500 |
| 3 | 7626120 | 4885580 | 12 | 7603300 | 4839140 |
| 4 | 7606860 | 4872750 | 13 | 7602590 | 4836620 |
| 5 | 7607200 | 4867420 | 14 | 7602620 | 4833080 |
| 6 | 7604850 | 4864780 | 15 | 7603020 | 4831910 |
| 7 | 7604770 | 4856700 | 16 | 7602230 | 4829100 |
| 8 | 7604160 | 4853590 | 17 | 7601200 | 4827130 |
| 9 | 7605420 | 4846380 | | | |

Figure 1. Location map of Timok valley with selected sample sites

A total of 51 water samples were collected from seventeen sampling points. Water samples were collected in three cycles of sampling, in July and October 2012 and April 2013., using 2000 ml plastic bottles. The sampling bottles for heavy metal determination were pre-soaked overnight with 10% HCl, rinsed with distilled water and then rinsed using river water before sample collection. Sampling bottles for the determination of physicochemical parameters were cleaned and rinsed using distilled water only. Preservation of water samples was done by adding 2 drops of concentrated $HNO_3$ to each water sample before storage below 4°C until they were analyzed.

The measured parameters were determined by the following methods: pH - potentiometric [16], electrical conductivity (ECw) - conductiometric [7], total dissolved solids (TDS) - gravimetric [4]. The acid-available fraction of heavy metals and other toxic elements (As, B, Cd, Cr, Cu, Hg, Fe, Ni, Pb, Zn) was determined using EPA 200.7 methods [10], as well as an ICAP 6300 ICP optical emission spectrometer (ICP-OES). The concentration of Hg was determined by a flame atomic adsorption analyzer SensAA Dual (GBC Scientific Equipment Pty Ltd, Victoria, Australia).

The experiment data were presented with mean of three tests with the presented summarized basic statistics of the dataset. Analysis of the interdependence of variables was carried out by calculating a linear Pearson correlation coefficients.

## Results and discussion

The seasonal and annual averages of physico-chemical characteristics are given in Table 1.

Table 1. Average values of the water quality parameters, along with the standard limits by irrigation water US and FAO and by Republic of Serbia

| Parameters | Mean±STDEV | Standard limits | | | |
|---|---|---|---|---|---|
| | | US irrigation water quality[10] | OfficialGazette, [18,19] | Ayers et al.[5] | Duncan et al. [8] |
| pH | 7.83±0.38 | 6.5-8.4 | | 6.5-8.4 | 6.0-9.0 |
| ECw 25˚C ($dSm^{-1}$) | 0.45±0.149 | <0.7 | <1.0# | <0.7 | |
| TDS ($mg·l^{-1}$) | 441.76±156.23 | <450 | | 0-2000 | |
| As ($mg·l^{-1}$) | 0.0046±0.0037 | | 0.05 | 0.1 | |
| B ($mg·l^{-1}$) | 0.069±0.09862 | | 1.0 | 0-2 | 2.0 |
| Cd ($mg·l^{-1}$) | 0.00037±0.00063 | 0.01 | 0.01 | 0.01 | |
| Cr ($mg·l^{-1}$) | 0.001079±0.0013 | 0.1 | 0.5 | 0.1 | |
| Cu ($mg·l^{-1}$) | 0.020±0.0471 | 0.2 | 0.1 | 0.2 | 0.2 |
| Fe ($mg·l^{-1}$) | 0.0813±0.1228 | 5.0 | | 5.0 | 5.0 |
| Ni ($mg·l^{-1}$) | 0.0057±0.01812 | 0.2 | 0.1 | 0.2 | |
| Pb ($mg·l^{-1}$) | 0.0032±0.0146 | 5.0 | 0.1 | 5.0 | |
| Zn ($mg·l^{-1}$) | 0.0102±0.0146 | 2.0 | 1.0 | 2.0 | 2.0 |
| Hg ($mg·l^{-1}$) | bdl | | 0.001 | | |

*References (listed below in reference list); bdl-below detection limit

ə - in me/l = mill equivalent per liter (mg/l ÷ equivalent weight = me/l); in SI units, 1 me/l=1 mill mol/liter adjusted for electron charge.

The pH value is a measure of basicity and acidity of the water (Figure 2). If the value is less than seven, the water or the aqueous solution is acidic, and if it is higher, then it is basic. Plants for growth and development favor the slightly acidic solution, the pH should be around 5.5. The pH is an important factor which determines the suitability of water for a variety of purposes, inter alia, for irrigation. The tested samples had pH values from neutral to slightly alkaline during the second cycle of sampling and showed a growing trend. This may be affected by drought and an increased flow of wastewater agriculture and households, as well as microbial activity.

Conductivity is a measure of the ability of an aqueous solution to carry an electric current. Increasing levels of conductivity and cations are the products of decomposition and mineralization of organic matter [1]. The aqueous salt solution and dissociated are broken down into positive and negative ions. Natural water are with electrical conductivity values generally less than unity. Measurement of the conductivity is performed at a specific temperature and it corresponds to the presence of dissolved salts. These are most commonly sodium chloride, and there may be also a sodium sulphate, calcium chloride, calcium sulfate, magnesium chloride, etc. Absolutely demineralized water does not conduct electricity, but even with small additions becomes a good conductor. Salts dissolved in the water increase its conductivity. In this study the conductivity was obtained by indirectly calculation of the amount of salt (Figure 3). According to all reference values (US, FAO and Republic of Serbia), the conductivity values of all samples showed good quality of this water for soil irrigation. Total dissolved solids (TDS) are an important characteristic for the determination of the quality of water for irrigation because it expresses the total concentration of soluble salts in water. Dissolved solids in water include all inorganic salts, silica and soluble organic matter. Pure water must be free from most suspended particles, which are responsible for turbidity. TDS was the highest in summer due to evaporation and reduced intake, which contributed to an increase in concentration, and was with the minimum value in the rainy season, due to the increased entry of rain and a corresponding reduction in concentration at all locations (Figure 4). The content of trace elements and heavy metals in the samples of water is generally below the MAC, maximum allowable concentration [19]. In sample No. 4 in the first series of sampling it was recorded an increased copper content (Figure 5) and above the MAC (0.2509 mg $l^{-1}$). Besides the vicinity of the village, with a sampling of wastewater gravitate to the sampling points, it is possible that the reason for the increased concentration is the use of a preparation based on copper. In the other series on this site it was not registered higher content of this element above the MAC. Sample No. 5, sampled in the second series (Figure 6) showed a slight increase in the nickel content above the MAC (0.124 mg $l^{-1}$) and how it is in the zone below the rural village, it is possible that this was caused by increasing anthropogenic activity, as in other series was not registered an increased content of this element.

The diversity in the results and demonstrated dynamic variations, suggests impact of a number of various environmental factors on the pattern of metals distribution in the water. In this regard [21], reported that the concentrations of metal ions strongly depend on the biological processes, redox potential, ionic strength, pH, the activity of organic and inorganic chelators and the purification processes in water.

By analyzing the correlation parameters, the conclusion is that there is a correlation between the samples and the characteristics of the water where the pH value has a significant negative correlation to all studied parameters except to the concentration of B [13]. ECw values were positively correlated to all studied parameters except to the concentration of Pb. TDS values showed a positive correlation to the concentration of B, Cu, Fe, Pb, Zn and negatively to the concentration of As, Cd, Cr, Pb in the samples of water. As, Cd, Cu, Fe, Pb and Zn each have a positive correlation which can be interpreted as they have the same potential sources of pollution; the correlation to other parameters is negative.

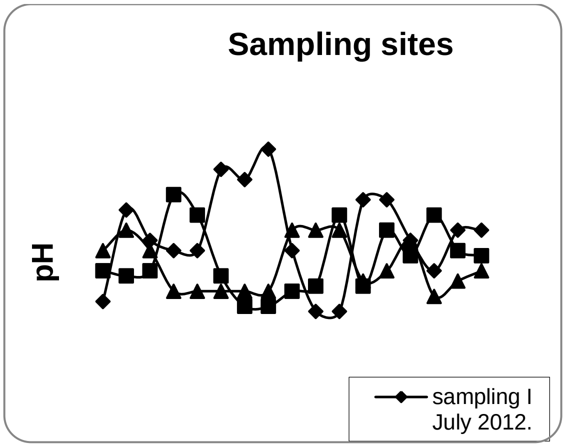


Figure 2. pH value of test water samples in batches of monitoring

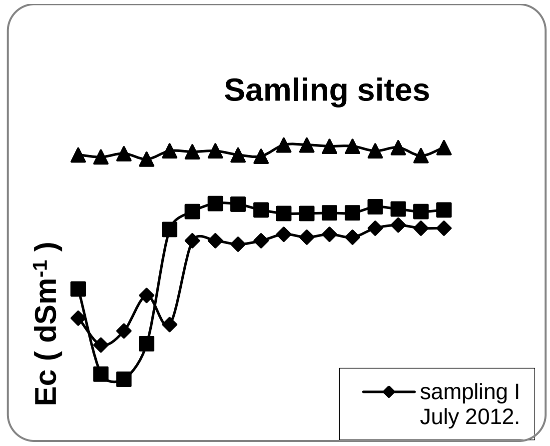


Figure 3. ECw value of test water samples in batches of monitoring

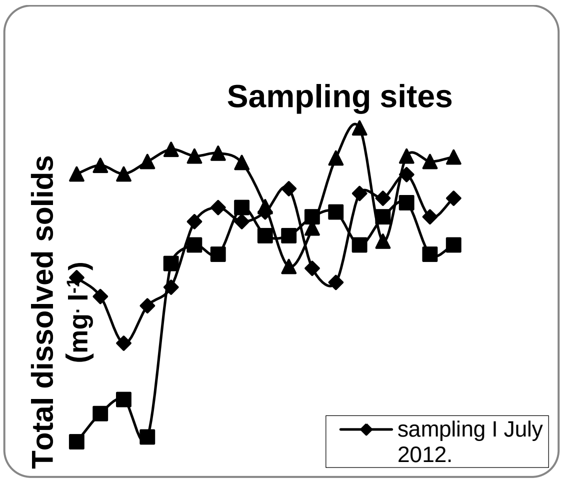


Figure 4. TDS value of test water samples in batches of monitoring

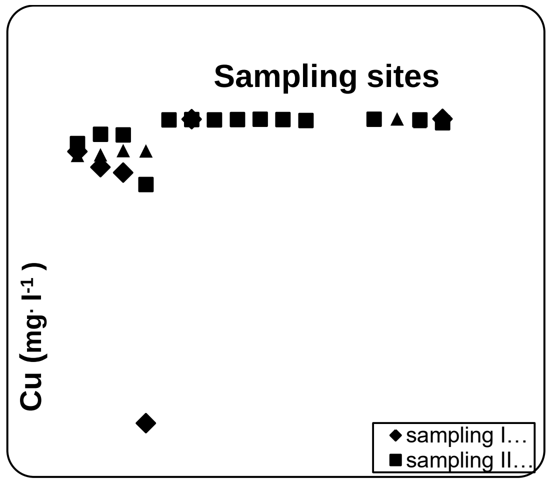


Figure 5. Cu concentration of test water samples in batches of monitoring

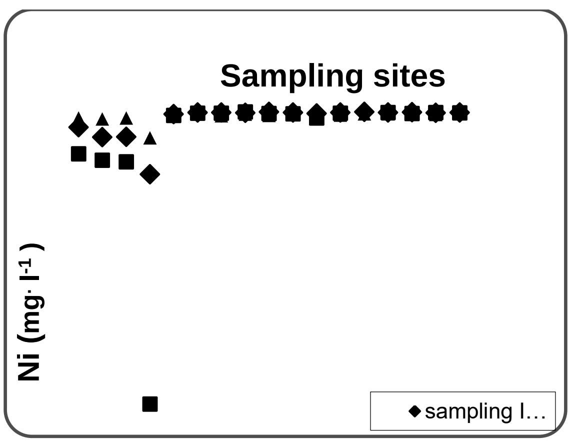


Figure 6. Ni concentration of test water samples in batches of monitoring

## Conclusion

Results from water samples showed that the content of heavy metals in the water of the Timok River in most of the samples analyzed in this study was within the MAC. Variations in the content of heavy metals in the water are the result of a wide range of human activities (primarily agriculture) in the study area and water levels throughout the year. Based on the presented it can be concluded that the water from Timok river can be used for irrigation of crops and soil in the vicinity of water flow to the restrictions and frequent quality checks during the summer months.

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## References

[1] B. Abida, R. Harikrishna, E-Journal of Chemistry, 5, (2):(2008):377-384.
[2] G. Antonović, V. Nikodijević, Đ. Tanasijević, Lj.Vojinović, N. Pavićević, Ž. Aleksić, Đ. Filipović, M. Jeremić : Zemljišta basena Timoka, Centar za poljoprivredna istraživanja, Institut za proučavanje zemljišta, Beograd (in Serbian) (1974).
[3] APHA Standard methods for the examination of water and wastewater. In A.E.(1992)
[4] A.E. Greenberg, L.S. Clesceri, A.D. Eato,(Eds.) American Public Health Association, 18$^{th}$ ed.,Washington, U.S.A.(1998)
[5] R.S. Ayers, D.W. Wescot: Irrigation and Drainage paper 29, Rev.1, (1994) 174 p.
[6] S.R.Carpenter, N.F.Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpley, V.H. Smith, Ecol Appl 8(3) (1998):559–68.
[7] Determination of electrical conductivity SRPS EN 27888:1993
[8] L.D. Doneen, D.W. Westcot: FAO.Irrigation practice and water management Irrigation and Drainage Paper 1, Rev. 1. FAO , (1988) Rome. 71 pp.
[9] R.R. Duncan, R.N. Carow, M. Huck. USGA Green Section Record: (2000)14-24
[10] EPA METHOD 200.7. (2001): Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry.
[11] FAO (1954). U.S. Salinity Laboratory Staff.
[12] O.S. Fatoki, N. Lujiza, O.A.Ogunfowokun, Water S.A. 28(2) (2005) pp.183.
[13] D. Gong, X. Gao, T. Ntakirutimana, J.Guo, K. Li, Pol J Environ Stud Vol. 22, No. 4, (2013)1061-1067.
[14] http://sh.wikipedia.org Accessed on 20/09/2017.
[15] H.P. Jarvie, B.A.Whitton, C. Neal, Sci Total Environ 210–211: (1998),79–109.
[16] Measurement of pH - Potentiometric method SRPS H.Z1.111:1987.
[17] D.W. Nelson, L.E. Sommers In: D. L. Sparks (Ed.), Methods of Soil Analysis, part 3 (SSSA, Madison, Wiskonsin, USA) 961 (1996).
[18] G. Konstandinova, N. Georgieva, Z. Yaneva, G. Petkov, M. Todorova, Ch.Miteva Bulg JAgric Sci, 19 (No 4) (2013), 635-643.
[19] Official Gazette of Republic of Serbia, (1994):23.
[20] Official Gazette of Republic of Serbia, (2012):50.
[21] H. Ozmen, F. Kulahc, A. Cukuroval, M. Dogru: Chemosphere, 55: (2004), 401–408.
[22] V.J. Simeonova, A. Stratis, C. Samara, G. Zachariadis, D. Voutsa, A. Anthemidis, M. Sofoniou, Th. Kouimtzis, Water Research 37 ( 2003), 4119–4124.
[23] World Reference Base for Soil Resources, 2014, http://www.fao.org/3/a-i3794e.pdf